(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 200 573
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 86303390.8

(22) Date of filing: 02.05.86

(51) Int. Cl.[4]: C 04 B 35/46
H 01 G 4/12

(30) Priority: 03.05.85 US 730711

(43) Date of publication of application:
05.11.86 Bulletin 86/45

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: TAM CERAMICS INC.
4511 Hyde Park Boulevard
Niagara Falls, NY 14305(US)

(72) Inventor: Chu, Mike S.H
714 Scovell Drive
Lewiston New York, 14092(US)

(72) Inventor: Hodgkins, Charles E.
457 Barton Drive
Lewiston New York, 14092(US)

(72) Inventor: Dean, Terrence C.
413 Lynnbrook Drive
Youngstown New York 14174(US)

(74) Representative: Crisp, David Norman et al,
D. YOUNG & CO. 10 Staple Inn
London, WC1V 7RD(GB)

(54) **Dielectric ceramic composition with high dielectric constant and flat TC characteristics.**

(57) The present invention provides ceramic compositions for preparing multi-layer capacitors (MLCs) having high dielectric constants between about 3000 and 4700 and stable temperature coefficients (TC) prepared from high purity barium titanate, niobium pentoxide and cobalt oxide.

EP 0 200 573 A2

Croydon Printing Company Ltd

Dielectric Ceramic Composition with High Dielectric Constant and Flat TC Characteristics

BACKGROUND OF THE INVENTION

This invention relates to ceramic dielectric compositions, preferably such compositions have high dielectric constants (K), e.g., between about 3000 and about 4700; low dissipation factors (DF), e.g., below about 2.5%; high insulation resistance (R) capacitance (C) products (RC), e.g. above about 5,000 ohm-farad at 25°C, above about 1000 ohm-farad at 125°C; and stable temperature coefficient (TC) in which the dielectric constant does not alter from its base value at 25°C by more than about 15 percent over a temperature range from -55°C to 125°C.

Multilayer ceramic capacitors (MLCs) are commonly made by casting or otherwise forming insulating layers of dielectric ceramic powder; placing thereupon conducting metal electrode layers, usually a palladium/silver alloy in the form of metallic paste; stacking the resulting elements to form the multilayer capacitor; and firing to densify the material thus forming a multilayer ceramic capacitor. Other processes for forming MLCs are described in U.S. Patents Nos. 3,697,950 and 3,879,645 the texts of which are incorporated herein by reference.

Barium titanate ($BaTiO_3$) is one of the major components most frequently used in the formation of the ceramic dielectric layers because of its high dielectric constant. However, the variation of the dielectric constant with temperature and the insulation resistance are also important factors to be considered in preparing ceramic compositions for use in multilayer capacitors. The electrical properties of many dielectric ceramic compositions may vary substantially as the temperature increases or decreases. Other factors also affect the electrical properties of ceramic compositions, e.g., insulation resistance may vary substantially based on grain sizes after final sintering.

In a desirable dielectric ceramic composition for use in a multilayer capacitor for applications requiring stability in the dielectric constant over a wide temperature range, the dielectric constant does not change from its base value at 25°C (room temperature) by more than about plus or minus 15 percent. The insulation resistance and capacitance product of such compositions should be more than 1000 ohm-farads at 25°C and more than 100 ohm-farads at maximum working temperature, 125°C in most cases. The method commonly used to produce such temperature stable capacitors consists of firing $BaTiO_3$ together with minor oxide additives for controlling the final dielectric properties. However, the dielectric ceramic compositions known in the art for making multilayer capacitors having stable TC characteristics usually have dielectric constants of not more than about 3000.

According to one aspect the present invention is directed to a dielectric composition having a high dielectric constant and stable TC characteristics comprising a major component comprising high purity barium titanate ($BaTiO_3$), and two minor components comprising niobium pentoxide (Nb_2O_5), and cobalt oxide (CoO). The barium titanate employed in this invention has purity exceeding about 99% with no individual impurity element greater than about 0.5%. Such high purity barium titanate can be produced via chemical coprecipitation processes and other techniques known in the art, e.g, by reacting high purity $BaCO_3$ and TiO_2 powders. The stoichiometry and the physical sizes of the barium titanate particles are controlled as hereinafter described to produce the desirable dielectric properties of the ceramic compositions of this invention. The preferred stoichiometric ratio for the barium titanate is BaO/TiO_2 of about 0.950 to 0.995 and the preferred average particle size is about 0.90 μm to 1.30 μm.

Other aspects of the invention are set forth in the claims.

More specifically, in forming the dielectric ceramic composition of the invention, the major component ($BaTiO_3$) comprises from about 97.70 to about 98.99 percent by weight and the minor components comprise from about 0.85 to about 1.69 percent by weight of Nb_2O_5 and from about 0.09 to about 1.20 percent by weight of CoO, with the Nb_2O_5 to CoO weight ratio from about 3.30 to about 18.00.

The ceramic compositions of this invention when formed into multilayer capacitors by conventional methods have dielectric constants which are typically between about 3000 and 4700 at 1KHz, 1VRMS, dissipation factors which are typically below about 3 percent at 1VRMS, and insulation resistance - capacitance products which are typically greater than about 5,000 ohm-farad at 25°C, 50 VDC/mil, greater than 1000 ohm-farad at 125°C, and stable TC characteristics in which the dielectric constant varies no more than about plus or minus 15 percent from its reference value at 25°C.

In an especially preferred embodiment, the ceramic dielectric composition is formed from a mixture of 98.82 weight percent of high purity $BaTiO_3$, 0.98 weight percent of Nb_2O_5 and 0.20 weight percent of CoO, with the Nb_2O_5 to CoO weight ratio being 4.90.

Because of their high dielectric constants, low dissipation factors, and stable TC characteristics, the ceramic compositions of this invention provide advantages in manufacturing multilayer ceramic capacitors, hereinafter called MLC's, such as high capacitance and small physical size. These advantages are very important for the capacitor manufacturing companies to meet the ever increasing demands of technology advance and cost reduction.

As hereinafter described in detail, the present invention provides a ceramic composition having a dielectric constant between about 3000 and 4700 at 25°C, a dissipation factor less than about 3%, and a stable temperature coefficient in which the dielectric constant does not vary more than about plus or minus 15 percent from its reference value at 25°C. The present invention also provides a ceramic composition suitable for manufacturing multilayer ceramic capacitors using precious metal internal electrodes and having the above properties as well as an insulation resistance - capacitance product of more than about 5000 ohm-farad at 25°C and more than about 1000 ohm-farad at 125°C.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As set forth below, the dielectric ceramic compositions of the present invention have several advantages which result in substantial technological advancement and cost savings without sacrificing desirable physical and electrical properties.

The present invention provides a novel dielectric ceramic composition having a dielectric constant between 3000 and 4700, and with stable TC characteristics which can be prepared by firing the component oxides or precursors thereof at a temperature between 1280°C and 1350°C. This composition differs substantially from those disclosed in the prior art in which desirable dielectric properties, such as a higher dielectric constant, are sacrificed in order to obtain materials which have stable TC characteristics. Since conventional materials have dielectric constants not more than about 3000, the use of the ceramic compositions of this invention in multilayer capacitors provides smaller devices with significantly higher capacitance values under the same physical size restriction, due to their much higher dielectric constants. Also because of their much higher dielectric constants, the use of the ceramic compositions of this invention in multilayer capacitors provides the smallest possible physical size under the same capacitance restriction. Also because of their much higher dielectric constants, the use of the ceramic compositions of this invention in multilayer capacitors results in significantly less ceramic and electrode material usage. With the ever increasing cost of precious metals, especially palladium, the manufacturing cost of MLC's can be significantly reduced with the present invention.

A fired ceramic body of the present invention is produced by reacting during the course of firing the constituent dielectric oxides of the ceramic preparation, including barium titanates, niobium pentoxide and cobalt oxide.

The preferred niobium pentoxide for use in this invention is about 99% pure and has a particle size of about

0.5 to 0.9 μm and the preferred cobalt oxide is about 70-74% pure and has a particle size of less than about 1 μm.

In preparing the ceramic preparation used in this invention, barium titanate, niobium pentoxide, and cobalt oxide in the proportions set forth above may be slurried together in water, or physically blended together. The mixture of the ceramic preparation may be mixed with a binder composition and cast into a sheet using standard methods, and formed into a multilayer capacitor structure with internal electrodes such as 70 percent palladium/30 percent silver, and fired at about 1280°C to 1350°C for about two hours.

Any conventional ceramic binder compositions may be used with this invention which is compatible with the other materials used and simply provides a vehicle for dispersing the ceramic particles and holding them together when the solvent is removed. Suitable binder compositions are described in "Ceramic Process Before Firing," G.Y. Onoda Jr., et al. John Wiley & Sons (1978) Chap. 19. Corn Syrup and Polyvinyl alcohol are examples of suitable binder compositions.

The fired dielectric composition of this invention has an insulation resistance-capacitance product (RC) greater than 5,000 ohm-farads at 25°C and 50 VDC/mil, and greater than 1000 ohm-farads at 125°C and 50 VDC/mil. The dielectric constant is typically between about 3000 to 4700 at 1 KHz and 1 volt rms, and the dissipation factor is typically less than 3.0 percent at 1 KHz and 1 volt rms.

The invention will be further illustrated by the following examples, but the invention is not intended to be limited thereto. The values given for the examples herein are subject to variations based on factors known in the art. For example, with respect to Examples 1-35 herein, the dielectric constant may be significantly increased and the dissipation factor may be significantly decreased by pulverizing, milling, uniformly dispersing, or otherwise reducing the starting materials to very fine particles. Such practices, which are commonly carried out in the course of manufacturing ceramic capacitors, were not employed to their full extent in the preparation of Examples 1-35. In addition, variations in firing conditions, sample thickness and preparation, and measurement error may result in differences in the observed values for the same composition. Thus, depending upon manufacturing techniques, and with little regard to particle size, the properties of ceramic compositions made using the proportions given in Examples 1-35 can vary from values given: for example the dielectric constants may vary by ± 100, the dissipation factor may vary by ± 0.2 percent, and the capacitance change with temperature versus capacitance at 25°C may vary by ± 1.5 percent.

Details of preferred embodiments of the present invention are further described in the following examples.

Examples 1-11

30 to 50 grams of ceramic compositions were prepared by adding high purity barium titanate ($BaTiO_3$), technical grade fine particle size niobium pentoxide (Nb_2O_5), and technical grade fine particle size cobalt oxide (CoO) according to the weight percent as shown in Table 1. The barium titanate employed in the above examples has BaO/TiO_2 stoichiometry of 0.986 and average particle size of 1.2µm. The ceramic powders were further blended with 15 to 25 cc of

distilled water and mixed thoroughly in a high speed Spex model 800-2 paint mixer manufactured by Spex Industries Inc., New Jersey for about 10 minutes. The wet slurry was then dried into a cake and ground with mortar and pestle. 2.4 to 4.0cc of a binder solution including 26 weight percent water, 26 weight percent propylene glycol and 48 weight percent corn syrup was mixed into the ceramic powder in a mortar and pestle which was then granulated through a 40 mesh nylon screen. Discs of the resultant mixture having a diameter of 1.27 cm and a thickness of 0.1 to 0.15 cm were pressed at a pressure of about 38,000 lbs per square inch in a stainless steel die. The discs were placed on a stabilized zirconia setter and fired at temperatures of 1280°C to 1340°C for 1 to 2 hrs. After cooling, silver electrodes were painted on the discs which were then fired at 815°C to sinter on the electrodes. The capacitance (C), the dissipation factor (DF), and the capacitance change with temperature versus capacitance at 25°C (TC) were then measured with a model ESI2110A capacitance bridge at 1KHz measurement frequency, from -55°C to +125°C at about 20°C intervals. The dielectric constant of each sample (K) was then calculated from the fundamental capacitance equation:

$$K = 5.66 \times C\frac{t}{D^2}$$

where K = dielectric constant of the sample
t = thickness of the disc in inches
D = diameter of the disc in inches
C = capacitance of the disc in pico farads

Table I

Example	$BaTiO_3$ Weight (%)	Nb_2O_5 Weight (%)	CoO Weight (%)	Ratio Nb_2O_5/CoO	Weight (%) Nb_2O_5+CoO
1	98.99	0.84	0.17	4.94	1.01
2	98.82	0.98	0.20	4.90	1.18
3	98.73	1.05	0.22	4.77	1.27
4	98.65	1.12	0.23	4.87	1.35
5	98.48	1.26	0.26	4.85	1.52
6	98.31	1.40	0.29	4.83	1.69
7	98.14	1.54	0.32	4.81	1.86
8	98.31	1.30	0.39	3.33	1.69
9	98.31	1.50	1.19	7.89	1.69
10	98.31	1.60	0.09	17.78	1.69
11	98.31	1.69	0.00	>>>>	1.69

The dielectric properties of Examples 1-11 as summarized in Table II demonstrate that, when Nb_2O_5 and CoO are added uniformly into the $BaTiO_3$ host material, ceramic compositions with dielectric constants greater than 3000 and with stable TC characteristics, such as Examples 2 to 10 are obtained. As will be demonstrated in later examples, both the dielectric constants and TC characteristics will be further improved when these ceramic compositions are cofired with silver/palladium internal electrodes in a MLC construction.

The dielectric data in Table II also shows that when the total Nb_2O_5 and CoO weight percent is less than about 1 wt.%, such as in Example 1, the ceramic composition has too negative a TC change at low temperatures and much higher DF although K is very high. When the Nb_2O_5 to CoO weight ratio is higher than 18.0, such as Example 11, TC becomes unstable and DF is high, although K is very high again.

Table II

Example	1KHz, 1VRMS K	DF(%)	TC (%) at -55°C	-30°C	85°C	125°C
* 1	4500	1.30	-27.1	-20.9	-7.3	+1.0
2	4030	0.93	-12.3	-7.5	-6.1	+6.6
3	3870	0.95	-8.2	-3.5	-5.1	+8.5
4	3765	0.85	-2.2	-0.5	-3.4	+11.1
5	3400	0.78	0.2	-1.4	-0.8	+14.6
6	3200	0.70	-2.6	-3.1	+0.8	+15.3
7	3025	0.75	-4.0	-4.0	+1.3	+16.2
8	4034	1.20	-22.5	-16.4	-13.7	-16.0
9	3377	1.20	-5.5	-4.0	-1.9	+9.4
10	3905	1.10	-23.2	-12.9	-11.0	-11.5
* 11	5895	4.3	-40.8	-27.9	-9.3	-16.0

Examples which are outside the scope of this invention, such as 1 and 11, will be labeled with "*" hereafter.

Examples 12-18

30 to 50 grams of ceramic compositions were prepared by adding high purity barium titanate, technical grade fine particle size niobium pentoxide, and technical grade fine particle size cobalt oxide, according to the weight percentages as shown in Table III. Fine particle size, high purity titanium dioxide (TiO_2), or barium oxide (added as barium carbonate ($BaCO_3$) were also added into the composition to adjust the BaO/TiO_2 stoichiometry. Ceramic disc samples were prepared, sintered, and dielectric properties measured with the same technique as described in Examples 1 to 11. The dielectric data as shown in Table IV demonstrate that when the

BaO/TiO_2 stoichiometric ratio is greater than 0.993 such as in Examples 17 and 18, the resulting ceramics have low dielectric constants and very high dissipation factors and therefore are not suitable for MLC applications. Although not shown in the data provided in Table III, when the BaO/TiO_2 ratio is less than 0.958 as in Example 15 the TC at -55°C tends to become much more negative. Past experience has also indicated that ceramic compositions with too large an excess TiO_2 have a tendency to develop nonuniform microstructures and poor reliability.

TABLE III

Example	$BaTiO_3$	Nb_2O_5	CoO	BaO	TiO_2	BaO/TiO_2
12	98.73	1.06	0.21	0	0	0.986
13	98.53	1.05	0.21	0	0.21	0.981
14	98.24	1.05	0.22	0	0.49	0.972
15	97.75	1.04	0.21	0	1.00	0.958
16	98.52	1.05	0.22	0.21	0	0.989
* 17	98.24	1.05	0.22	0.49	0	0.993
* 18	97.77	1.04	0.21	0.97	0	1.001

TABLE IV

Example	K	DF(%)	[TC (%) at] -55°C	-30°C	85°C	125°C
12	3700	0.90	-4.3	-1.7	-3.6	+12.4
13	3800	0.97	-9.5	-3.5	-6.5	+6.9
14	3870	0.96	-12.5	-5.7	-7.3	+4.2
15	4010	0.93	-13.8	-7.1	-8.3	+2.2
16	3680	0.90	-4.6	-1.7	-3.2	+13.3
* 17	3590	1.50	-8.2	-4.3	-5.4	+9.2
* 18	3250	2.90	-14.6	-14.5	-12.6	+3.6

Example 19-21

500 grams of high purity $BaCO_3$ and 202 grams of high purity TiO_2 are thoroughly mixed and dispersed in about 175cc of deionized water until a uniformly dispersed slurry is obtained. Up to 4 weight percent "DARVAN C"1/ may be added into the slurry to help to disperse the powder particles. The slurry is then discharged into a drying pan and dried in an oven at about 150°C with forced air circulation. The dried cake is then pulverized, loaded into a ceramic sagger, and calcined at temperature from about 1900°F to about 2200°F for about 1 hour to 5 hours. X-ray diffraction and BaO alkalinity tests on the examples indicated complete reaction and formation of high purity $BaTiO_3$. The calcined powder was then vibratory energy milled with ZrO_2 media until the average particle size was reduced to less than 1.2 µm. It will be obvious to those skilled in the art that particle size reduction can also be achieved by alternative methods, e.g., ball milling, and that the milling media can be any compatible

1 DARVAN C is a alkali ion free aqueous dispersing agent comprising a mixture of polyelectrolytes, ammonia and sulfur available from W.P. Vanderbilt Co., Conn.

wear resistant material such as ZrO_2, zircon, alumina, or the like. Another alternative method for reducing particle size is jet milling with compressed air without media. Whatever process might be selected, the critical requirement is that it does not contaminate the ceramic powder, e.g., with significant media wear. 30 to 50 grams of ceramic compositions according to the weight percents as shown in Table V are prepared and their dielectric properties measured with the same technique as described in Examples 1 to 11. The dielectric data as shown in Table VI demonstrates that the high purity $BaTiO_3$ prepared in accordance with the present invention provides ceramic compositions with high dielectric constants and stable TC characteristics. The dielectric performance of these examples is similar to those as demonstrated in Examples 2 to 10.

TABLE V

	Weight (%)			Ratio	Weight(%)
Example	$BaTiO_3$	Nb_2O_5	CoO	Nb_2O_5/CoO	Nb_2O_5+CoO
19	98.65	1.12	0.23	4.87	1.35
20	98.60	1.14	0.26	4.38	1.40
21	98.53	1.19	0.27	4.41	1.46

TABLE VI

			TC(%) at			
Example	K	DF(%)	-55°C	-30°C	85°C	125°C
19	3520	0.94	-1.3	-1.5	-3.6	+13.4
20	3700	1.18	-20.2	-13.9	-13.0	-2.9
21	3500	1.09	-15.2	-9.2	-11.4	+1.1

Examples 22-29

Batches of about 4.5 kilograms or about 270 kilograms of ceramic compositions were prepared for Examples 22-29 by blending and mixing high purity barium titanate, technical grade fine particle size cobalt oxide and niobium pentoxide in twin shell blenders, manufactured by Patterson - Kelley Co., E. Stroudsburg, PA, according to the compositions shown in Table VII.

TABLE VII

	Weight (%)				
Example	$BaTiO_3$	Nb_2O_5	CoO	Nb_2O_5+CoO	Electrode Material
22	98.31	1.40	0.29	1.69	70Pd/30Ag
23	98.61	1.15	0.24	1.39	70Pd/30Ag
24	98.82	0.98	0.20	1.18	70Pd/30Ag
25	98.72	1.06	0.22	1.28	70Pd/30Ag
26	98.72	1.06	0.22	1.28	100Pd
27	98.72	1.06	0.22	1.28	40Au/40Pt/20Pd
28	98.72	1.06	0.22	1.28	100Pt
29	98.72	1.06	0.22	1.28	No electrodes

400 grams of the above uniformly blended ceramic compositions was then charged into a ball mill with 1/2 inch alumina media together with 218 grams of a binder solution made by uniformly mixing and dissolving 186 grams dioctylphthalate, 90 grams Nuostabe V-1444,[2/] 597 ml ethanol, 270 ml toluene, and 372 grams Butvar B-76[3/] vinyl resin.

---

2 Nuostabe V-1444 is an alkali ion free organic solvent dispersing agent available from Nuodex Co. Inc., New Jersey.

Other compatible binders may be used such as those binders described in "Ceramic Processes Before Firing" Id.

This slurry was milled for 16 hours, discharged, and filtered through a 44 micron screen. This slurry, having a viscosity of about 1500 to 3000 centipoise, was then de-aired and cast, in accordance with standard techniques, into a tape with a thickness of 1.5 mils. The tape was converted into multilayer ceramic capacitors having 70 percent Palladium/30 percent silver; 100 percent Palladium; 40 percent gold/40 percent platinum/20 percent palladium; or 100 percent platinum electrodes via conventional processes well known in the industry. Samples with no electrodes at all were also prepared for purposes of comparison. The capacitors were preheated to 260°C for 48 hours, placed on stabilized zirconia setters and sintered at 1280°C to 1350°C for 2 hours. The sintered capacitors had 10 active dielectric layers with dielectric thickness ranging from 0.85 to 1.10 mil. Termination electrodes of DuPont Silver paint No. 4822, which is a mixture of silver and glass frit in a binder, were applied at opposite ends of the multilayer capacitor to connect alternate electrode layers and these capacitors were fired at 815°C in a tunnel furnace, the dielectric constant (K), dissipation factor (DF), insulation resistance (R) and capacitance (C) product (RC) at 25°C, and 125°C, and capacitance change with temperature (TC) versus capacitance at 25°C were measured with the same instruments described in Examples 1 - 11. The results are shown in Table VIII below. The measurements were again performed from -55°C to 125°C in

---

3 Butvar B-76 is a binder comprising a mixture of polyvinyl butyral, polyvinyl alcohol and polyvinyl acetate available from Monsanto Corp.

20°C increments.

The dielectric properties of Examples 22 - 29 as summarized in Table VIII demonstrate that multilayer ceramic capacitors manufactured from ceramic compositions of this invention have high dielectric constants, greater than 3500 and up to 4800, low dissipation factor, less than 2%, very stable TC characteristics, and high insulation resistance - capacitance products, greater than 4000 at 25°C and greater than 2000 at 125°C. The dielectric properties of these MLC's all meet and exceed the requirements listed in the EIA (Electronic Industries Association) specification for X7R ceramic multilayer capacitors. For X7R, such specification demands that the capacitors meet the requirement of dissipation factor less than 3%, RC product greater than 1000 at 25°C and greater than 100 at 125°C, and TC within ± 15% from -55°C to 125°C.

Of particular importance to the ceramic compositions of this invention are the improved dielectric properties, particularly the dielectric constant and the TC at low temperatures which may be further improved when the ceramics are cofired with internal electrode materials in manufacturing the MLC's.

TABLE VIII

Example	22	23	24	25A	25B
Electrode	70Pd/30Ag	70Pd/30Ag	70Pd/30Ag	70Pd/30Ag	
Dielectric Thickness (mils)	0.90	1.00	0.85	1.0	4.1
K at 25°C	3525	3840	4770	4190	4210
DF at 25°C (%)	1.41	1.51	1.74	1.68	0.90
TC at -55°C (%)	+7.4	+9.1	-0.2	+3.8	-2.3
-30°C (%)	+2.6	+6.4	+2.2	+5.5	0.34
85°C (%)	-3.1	-5.7	-10.9	-10.3	-7.7
125°C (%)	+5.9	+2.0	-7.8	-6.7	+4.2
RC at 50V/mil					
at 25°C	4130	5435	5135	6380	8645
125°C	3025	3025	3910	3480	4710

Example	26	27	28A	28B	29
Electrode	100Pd	40Au/40Pt 120Pd	100 Pt		No Electrodes
Dielectric Thickness (mils)	1.00	1.00	1.00	3.84	20
K at 25°C	3750	4105	3410	3710	3660
DF at 25°C (%)	1.48	1.60	1.80	1.13	0.74
TC at -55°C (%)	+5.1	+4.8	+4.2	-0.13	-3.8
-30°C (%)	+4.5	+3.3	+2.0	-0.05	-0.4
85°C (%)	-6.7	-5.9	-5.1	-3.70	-5.8
125° (%)	4.9	+6.7	+7.6	+11.2	+8.4
RC at 50V/mil					
at 25°C	6500	5035	5180	7830	____
125°C	5000	3000	2300	4200	____

Examples 30-31

About 900 kilograms of ceramic composition were prepared by blending and mixing in the same manner as described in Examples 22-29 according to the compositions as shown in Table IX. Multilayer ceramic capacitors were made and their dielectric properties were measured in the same manner as described in Examples 22-29. The results as summarized in Table X demonstrate that multilayer capacitors made from ceramic compositions of these examples also have high dielectric constants, low dissipation factors, high insulation resistance, and stable TC characteristics meeting EIA's X7R specification.

TABLE IX

Weight (%)

Example	$BaTiO_3$	Nb_2O_5	CoO	Nb_2O_5+CoO	Electrode Material
30	98.56	1.17	0.27	1.42	70Pd/30Ag
31	98.67	1.08	0.25	1.33	70Pd/30Ag

TABLE X

Example	30	31
Electrode	70Pd/30Ag	70Pd/30Ag
Dielectric Thickness (mils)	0.98	1.30
K at 25°C	4850	3831
DF at 25°C (%)	2.24	2.15
TC at -55°C (%)	+6.5	-3.3
-30°C (%)	+4.0	+1.0
85°C (%)	-7.0	-12.2
125°C (%)	+2.5	-4.0
RC at 50V/mil		
at 25°C	74700	6810
125°C	21370	5270

Examples 32-35

About 500 grams of the ceramic composition of Example 29 were added with about 350cc of deionized water and about 5 grams of DARVAN C dispersing agent. Table XI shows the average particle size and the dielectric composition of Examples 32-35. The powder was then ball milled with zirconia milling media in a rubber lined milling jar for about 10 to 40 hours until the average particle sizes were 1.27, 1.20, 0.8, and 0.6 μm respectively. Subsequent chemical analysis indicate no impurity pick up from the zirconia media. Ceramic discs were prepared and their dielectric properties measured in the same manner as described in Examples 1 to 11. The data as shown in Table XII demonstrate that even with the same ceramic composition, the control of proper particle size distribution to obtain desirable electrical properties is important. When the average particle sizes are less than 0.8 µm, such as in Examples 34 and 35, the TC at both the cold and hot temperature side are much too negative, and the dissipation factors are very high, although the dielectric constant is very high. These ceramic compositions are outside the scope of this invention. Based on previous art and experience compositions with average particle sizes larger than 1.30 µm, are also not desirable because such compositions are usually difficult to sinter to full density which causes lower dielectric constants and higher dissipation factors.

TABLE XI

		Weight (%)		
Example	Average Particle Size(µm)	$BaTiO_3$	Nb_2O_5	CoO
32	1.27	98.56	1.17	0.27
33	1.20	98.56	1.17	0.27
* 34	0.80	98.56	1.17	0.27
* 35	0.60	98.56	1.17	0.27

TABLE XII

TC (%)			TC(%) at			
Example	K	DF(%)	-55°C	-30°C	85°C	125°C
32	3500	1.13	-4.0	-3.5	-3.5	+17.4
33	3730	0.95	-8.3	-3.4	-8.2	+8.6
* 34	4570	1.52	-30.3	-22.6	-18.3	-19.1
* 35	4500	1.70	-34.5	-24.9	-11.3	-22.1

CLAIMS:

1. A ceramic composition, comprising:
about 97.70 - 98.99 % wt barium titanate;
about 0.85 - 1.69% wt of niobium pentoxide;
about 0.09 - 1.20% wt of cobalt oxide;
and a wt ratio of niobium pentoxide to cobalt oxide of about 3.30 to 18.00.

2. The ceramic composition of claim 1, wherein:
the barium titanate has a purity of about 99.0%, a BaO/TiO_2 stoichiometric ratio of about 0.950 to 0.995; and an average particle size of about 0.90μm to 1.30μm.

3. The ceramic composition of claim 2, wherein:
the niobium pentoxide has a purity of about 99.0% and a particle size of about 0.5 to 0.9μm; and
the cobalt oxide has a purity of about 70% to 74% and a particle size of less than about 1.0 μm.

4. The ceramic composition of claim 1 wherein:
the barium titanate comprises about 98.82 % wt;
the niobium pentoxide comprises about 0.98% wt;
the cobalt oxide comprises about 0.20% wt; and
the niobium pentoxide to cobalt oxide weight ratio is about 4.90.

5. A ceramic composition for making MLCs having high dielectric constants and TC characteristics that vary no more than about + 15 percent from their reference value at 25°C over a temperature range of -55°C to 125°C, the composition comprising a mixture of:

about 97.70 - 98.99 % wt barium titanate;

about 0.85 - 1.69 % wt of niobium pentoxide;

about 0.09 - 1.20 % wt of cobalt oxide;

having a weight ratio of niobium pentoxide to cobalt oxide of about 3.30 to 18.00; and

the mixture dispersed in a binder composition.

6. The ceramic composition of claim 5, wherein:

the barium titanate has a purity greater than about 99.0%, the BaO/TiO_2 stoichiometric ratio is about 0.950 to 0.995, and an average particle size is about 0.90µm to 1.30µm.

7. The ceramic composition of claim 6, wherein:

the niobium pentoxide has a purity of about 99.0% and a particle size of about 0.5 to 0.9µm; and

the cobalt oxide has a purity of about 70% to 74% and a particle size of less than about 1.0 µm.

8. The ceramic composition of claim 5, wherein:

the barium titanate comprises about 98.82% wt;

the niobium pentoxide comprises about 0.98% wt;

the cobalt oxide comprises about 0.20% wt; and

the niobium pentoxide to cobalt oxide weight ratio is about 4.90.

9. A MLC prepared with the composition of any one of claims 1 thru 8 and cofired with at least one metal selected from the group consisting of silver, gold, platinum and palladium.

10. A method for preparing MLCs having dielectric constants between about 3000 and 4700 and stable TC's which comprises the steps of:

(a) forming a plurality of dielectric layers from a mixture comprising:

about 97.70 - 98.99 % wt barium titanate;

about 0.85 - 1.69 % wt of niobium pentoxide;

about 0.09 - 1.20 % wt of cobalt oxide;

and a wt ratio of niobium pentoxide to cobalt oxide of about 3.30 to 18.00;

(b) compressing and firing the mixture; and

(c) forming a plurality of electrodes between the dielectric layers.

11. The method of claim 10, wherein:

the barium titanate has a purity of about 99%; a BaO/TiO_2 stoichiometric ratio of about 0.950 to 0.995; and an average particle size of about 0.90 µm to 1.30 µm.

12. The method of claim 11, wherein:

the niobium pentoxide has a purity of about 99.0% and a particle size of about 0.5 to 0.9µm; and

the cobalt oxide has a purity of about 70% to 74% and a particle size of less than about 1.0 µm.

13. The method of claim 10, wherein:

the barium titanate comprises about 98.82% wt;

the niobium pentoxide comprises about 0.98% wt;

the cobalt oxide comprises about 0.20% wt; and

the niobium pentoxide to cobalt oxide weight ratio is about 4.90.